INVESTIGATION OF THE MAGNESIUM ANODE

THIRD QUARTERLY PROGRESS REPORT

1 JANUARY 1962 TO 31 MARCH 1962

SIGNAL CORPS CONTRACT NO. DA36-039-SC-88912

DEPARTMENT OF ARMY TASK NO. 3A99-09-001-02

U. S. ARMY SIGNAL RESEARCH AND DEVELOPMENT LABORATORY

FORT MONMOUTH, NEW JERSEY

THE DOW METAL PRODUCTS COMPANY

DIVISION OF THE DOW CHEMICAL COMPANY

MIDLAND, MICHIGAN

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BEHAVIOR OF THE MAGNESIUM ANODE

Prepared by: J. L. Robinson

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I. PURPOSE

The purpose of this research and development contract is the study of phenomena occurring when magnesium is utilized as an anode. The aim is to gain a better understanding of the basic electrochemistry involved in the use of magnesium in primary battery systems.

The work falls into the broad areas listed below:

A. Anode Dissolution (Efficiency)

    1. Continuous Anode Current

    2. Intermittent Anode Current

B. Anode Polarization

    1. Transient ("Delayed Action")

    2. Steady State

The amount of effort expended in a given area will be dependent upon the results of preliminary investigations in the various areas.

II. ABSTRACT

The "maximum anode efficiency" was found to be independent and the open circuit corrosion dependent on the relative acidity of the electrolyte. Anode efficiency was decreased by chloride ion contamination with acetate and perchlorate electrolytes. Acetate and perchlorate ions were compatible in a mixed electrolyte. The effectiveness of chromate inhibition was current density dependent with acetate electrolyte. The critical current density for anode polarization varied inversely with the electrolyte concentration. The effect of anode composition on polarization was dependent upon the electrolyte employed.

III.   CONFERENCES

On January 30, 1962, Mr. Donald Wood of the U. S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey, visited The Dow Metal Products Laboratory at Midland, Michigan to discuss the progress of this contract.

Mr. J. L. Robinson and Dr. M. R. Bothwell represented The Dow Metals Products Company.

IV. DATA AND DISCUSSION

(A-1) Anodic Dissolution - Continuous Current

A. Anode Efficiency - Various Salts

The anode efficiency behavior of AZ21X1 anodes in a few additional environments was investigated. The electrolytic cell, procedure for efficiency measurements, and method of determining the maximum available efficiency have been discussed in Reports Nos. 1 and 2. The new data obtained are shown in Table I. In Report No. 2 it was pointed out that the current density for maximum efficiency was specific to the particular electrolyte and its concentration. This was again observed.

A relationship between the "maximum efficiency" and the relative acidity of the environment might be expected since the protective film on magnesium is essentially magnesium hydroxide. Such a relationship apparently does not exist. There is a marked increase in the relative acidity of the bulk electrolyte in respect to magnesium hydroxide in going from calcium acetate to magnesium acetate to ammonium acetate, but the same "maximum efficiency" was observed for all three electrolytes. It was previously noted that the "maximum efficiency" could not be related to the strength of the parent acid, Report No. 2.

It is assumed that the low efficiency obtained with cobaltous acetate was due to high local corrosion resulting from the deposition of cathodic cobalt on the anode. This electrolyte was tested because of its acidic nature, which is comparable to that of ammonium acetate,

and the high activity coefficients[1] associated with some cobalt salts at high concentrations.

The decrease in the maximum efficiency to less than 80 per cent with magnesium formate electrolyte demonstrates that the radical attached to the carboxyl group can be important in determining efficiency behavior with electrolytes of salts of carboxylic acids. That the aromatic radical is not detrimental was demonstrated by the high efficiency measured with the potassium salicylate electrolyte. The potential behavior observed with this latter electrolyte was unique. If the anodic current was applied within a couple of minutes after immersion of the anode in the electrolyte the potential moved sharply passive. However, if a soak time of fifteen minutes was allowed, the potential remained active in the region of -1.35 volts vs. saturated calomel with the application of current. There was no marked increase in the activity of the anode during the soak period in respect to either the open circuit potential or the visible amount of hydrogen being liberated.

It is planned to complete the survey of the efficiency behavior with salts of the various classes of acids during the next quarter.

B.   Mixed Electrolytes

The following advantages or disadvantages results from the use of salts of some organic acids in place of salts of inorganic acids for electrolytes with magnesium anodes:

1.   The portion of the anode coulombic capacity available

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for useful work is increased from the 65 to 75% range to the 90 to 95% range.

2. The distribution of anode consumption is highly uniform as opposed to a preferential attack pattern.

3. The anode is more susceptible to polarization.

4. There is an appreciable increase in the electrolyte resistivity.

It would be desirable to wed the best features of the electrolytes of organic and inorganic salts. The following investigations were aimed at obtaining an initial indication of the prospects for such combinations:

1. Mixed Acetate - Chloride Electrolytes

The anode efficiency was measured with a 2 normal magnesium acetate electrolyte to which varying small amounts of magnesium chloride were added. The results are shown in Table II. The efficiency behavior appeared to be completely determined by the chloride ion when the Ac^-/Cl^- ratio was decreased to four. The corrosion pattern resembled that observed with chloride rather than that with the acetate electrolytes when the Ac^-/Cl^- ratio reached 200. Thus, chloride ion can not be used to activate or increase the conductivity of acetate type electrolytes. The results do confirm that the low efficiencies observed with the chloroacetates, Report No. 2, were due to the chloride ion contamination.

2. Mixed Acetate - Perchlorate Electrolytes

The limited data obtained are shown in Table III. The

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efficiency behavior appears to be dominated by the acetate ion even in the presence of high levels of perchlorate ion. The corrosion pattern was intermediate between that observed with each ion alone. This suggests that acetate and perchlorate could be combined in one electrolyte. Additional data are needed to evaluate the desirability of such a combination.

The chloride ion contamination of the above perchlorate salt was reduced prior to its use by treating a stock solution with silver perchlorate, adding zinc and magnesium powders to scavenge the excess silver ions, and filtering. It was not determined that this precaution was required.

3.   Perchlorate Contamination With Chloride Ion

From the past data an anode efficiency in the range of 75% can be expected with AZ21 anodes, 2 normal $Mg(ClO_4)$, and a current density of 15 milliamperes per square centimeter. However, efficiencies as low as 40% were obtained when a new lot of $Mg(ClO_4)_2$ salt was used for the electrolyte. It was suspected that the low efficiencies were caused by higher than normal chloride contamination with this lot of salt. Analysis showed a .01 normal chloride ion concentration in a 6 normal perchlorate solution. This chloride level could not be directly compared with those of previous lots of per-chlorate since they had been consumed. However, the expected effi-ciencies were obtained thru reduction of the chloride level by the method outlined above, Table IV. The extremely low efficiencies (39%) of Alloy No. 91223, Table IV, and also the 39% efficiency reported

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previously (Report No. 2) for an AZ10XA composition were due to inter-granular corrosion. Normal corrosion was observed with Alloy No. 91233, AZ21X1, with the treated electrolyte.

The low efficiency with AZ10XA composition was obtained with one of the original lots of $Mg(ClO_4)_2$ which presumbly had less chloride contamination. This composition has not been investigated with a treated electrolyte. Photomicrographs of the intergranular corrosion are shown in Figure 1. A minimum anode efficiency in the region of 1.0% aluminum was reported for a Mg-Al binary series, Report No. 2. A detailed microscopic examination failed to relate this minimum efficiency to the type of corrosion.

 C. Open Circuit Dissolution

A preliminary investigation of the open circuit corro-sion behavior of AZ21X1 in a few electrolytes was undertaken. The test consisted merely of seven day stagnant immersion in approximately 8cc of electrolyte per square centimeter of sample. The corrosion rates were calculated as milligrams of weight loss per square centi-meter per day (MCD). Tests were run with and without chromate inhibitor. Data obtained are shown in Table V. The corrosion rate increased with increasing electrolyte acidity (increasing magnesium ion concentration or the substitution of ammonium ion for the magnesium ion). This is consistent with the past experience of our laboratory. Chromate appears to be an effective inhibitor only at extremely low current densities with acetate electrolyte. A corrosion rate of one MCD is equivalent to an anodic current density of $0.092MA/cm^2$. Chromates failed to inhibit the corrosion when the inherent rate reached 1.2 MCD, Table V.

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That the inhibition is current density dependent was demonstrated with the 3N Mg(Ac)$_2$ electrolyte. The open circuit corrosion rate was reduced from 0.13 to 0.013MCD by the Na$_2$CrO$_4$ addition with this electrolyte, Table V. The anode efficiency, which reflects the wasteful corrosion rate, was not affected by the chromate addition even at a current density as low as 0.3MA/cm^2 which is equivalent to an artificial corrosion rate of 3MCD. Further, one could see the chromate being reduced at sites of hydrogen evolution forming black chromic-chromate needles rather than forming a film. These needles would grow out from the anode face to lengths of 1/4 of a inch before dropping to the bottom of the cell.

(B-2)   Steady State Polarization

A.   Anode Polarization Parameters - Wet Cells

The procedure employed for the below polarization studies was discussed in Reports Nos. 1 and 2.

With application of increasing currents the anode suffers a transient polarization from which the potential recovers to the region of its original or open circuit value[2]. It was pointed out in Report No. 2 that anode potential could again move sharply in the passive direction with continuing passage of the current after completion of this transient polarization, Figure 2. It was further noted that over a limited range the current density and time to this latter polarization could be related by the following equation:

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$$\frac{1}{T} = k \ (i_a - i_c) \hspace{4cm} (1)$$

where T = time for 1 volt polarization i_a = applied current density,

and i_c and k are constants.

This is the relationship expected for polarization caused by protective film formation. The constant i_c represents the maximum rate of film breakdown expressed as a critical current which must be exceeded prior to any film build-up. The reciprocal of constant k represents the coulombs needed to deposit the protective film. Plotting the data in accordance with equation (1) results in two polarization parameters: (a) The critical current density which is the intercept and (b) the coulombs needed to deposit the film which is the reciprocal slope, Figure 4.

B.   Reproducibility of Data

Figure 2 is a typical potential-time plot for acetate and halide type electrolytes. With such electrolytes the potential is stable up to about 10 volts passive. With perchlorate electrolyte the potential cycles is a few hundreds of a volt in the active region even with small applied anodic current, and by as much as 0.5 volts when the current is sufficiently large to cause a 1 volt polarization, Figure 3. Figures 4 and 5 are typical plots of the reciprocal time for one volt polarization vs. current density for acetate and chloride electrolytes respectively. The scatter encountered with perchlorate electrolyte was comparable to that observed with halide, Figure 5.

C.   Effect of The Electrolyte Salt On Polarization Parameters

The polarization parameters for 6N $Mg(ClO_4)_2$ and AZ21X1

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anodes were obtained from the plot of the data of Table VI and compared to those for $Mg(Ac)_2$ and $MgCl_2$ (Report No. 2) in Table VII. The critical current density is highly dependent upon the specific electrolyte salt. It was suggested in Report No. 2 that the coulombs needed to form the protective film were relatively independent of the environment. That this is not valid is shown by the values in Table VII.

D.   Effect of Electrolyte Concentration On Polarization

The times to one volt polarization at various current densities and concentrations of $Mg(Ac)_2$ are tabulated in Tables VIII, IX, and X. The polarization parameters obtained from the plots of these data are listed in Table XI. The critical current density is inversely proportional to the concentration, Figure 6. The measured concentration of saturated $Mg(Ac)_2$ was 7.9 normal. The concentration for zero critical current was 8.4 normal from extrapolation of the curve, Figure 6. The precipitation of $Mg(Ac)_2$ at the anode as the cause of the polarization is suggested by the agreement between these concentrations for saturation and zero critical current density. However, the coulombs needed for simple precipitation, which should be relatively independent of electrolyte concentration, ranged from 0.6 to 4.8 with no apparent orderly dependence on concentration, Table XI. The increase in critical current density with decreasing concentration was also observed with $MgCl_2$ and $Mg(ClO_4)_2$ electrolytes. An oscilliscope had to be used to follow the potential-time behavior at low concentrations (3 normal) with these electrolytes because of the short times and high currents involved. Insufficient data were

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obtained to determine the actual magnitudes of the polarization para-
meters at the 3 normal concentration.

E.   Effect Of Anode Composition On The Polarization Parameters

The times to one volt polarization with various current
densities, electrolytes, and anode compositions are tabulated in
Tables XII through XVII. The polarization parameters obtained from
the plots of these data are shown in Table XVIII. The effect of alloy-
ing agents is specific to the electrolyte employed. For example,
the critical current density was not effected with $MgCl_2$ electrolytes,
but did decrease from 0.028 to 0.014 amperes per square centimeter
with $Mg(Ac)_2$ electrolyte as the calcium content of the anode increased
from <0.01 to 0.14 per cent, Table XVIII. It was suggested above that
the critical current density is directly related to the maximum rate
of film breakdown. It would be reasonable to expect that maximum
efficiency to increase as the critical current decreases since increased
efficiency should result from decreased protective film damage. Actu-
ally, the opposite effect was observed with a given electrolyte. For
example, with the acetate electrolyte both the critical current
(Table XVIII) and the maximum anode efficiency (Report No. 2) decreased
with increasing aluminum content.

V. CONCLUSIONS

The relative acidity of the electrolyte to $Mg(OH)_2$ does not effect the "maximum anode efficiency".

Chloride ion contamination is detrimental with acetate and perchlorate electrolytes.

Acetate and perchlorate ions are compatible in an electrolyte.

Chromate inhibition of acetate electrolyte is effective only at extremely low current densities.

The anode polarization observed in wet cells is due to complex, protective film formation.

VI.   TENTATIVE PROGRAM, FOURTH QUARTER

The program for the fourth quarter will be largely aimed at consolidating observations to date.

Efficiency and potential behavior with representative salts of the various classes of organic acids will be screened.

The feasibility of a mixed acetate-perchlorate electrolyte will be further explored.

The suggested (Report No. 2) direct relationship between the critical current density for anode polarization and the current density for maximum anode efficiency will be investigated.

The effect of temperature on polarization parameters will be determined.

A few cells will be fabricated to determine if some of the desirable features of acetate electrolytes which were observed in wet cells carry over to dry cells.

VII. REFERENCES

1. Parsons, "Handbook of Electrochemical Constants", Butterworths Scientific Publications, London, 1959.

2. J. L. Robinson and P. F. King, "J. Electrochem. Soc.", 108, 36, (1961).

EFFICIENCY BEHAVIOR—VARIOUS ELECTROLYTES

AZ21X1 ANODES—70°F

ELECTROLYTE SALT	NORMALITY	% ANODE EFFICIENCY CURRENT DENSITY—MILLIAMPERES PER CM^2							
		1.5	9.3	16	23	31	39	45.6	MAX. EFF.
Mg(AC)2	1	77	90	89	85	79		73	90
NH4AC	1		63	84	86	89		87.5	90
"	9.6		83	84.5	85.5	76.5		81	86
Co(AC)2	2					(1)43			
Ca(AC)2	1		89	88	86	78		68	90
CALCIUM FORMATE	1		61	67	60	77		76	78
"	2	53	60	70		77			78
"	SATURATED		61	67	78	77	77.5	76.6	79
POTASSIUM FORMATE	1		61	67	71	74		74.5	76
"	6		74	72	72	71		72	76
"	10		78	78	78.3	78.8		78.8	79
POTASSIUM SALICYLATE	1		(2)88						

(1) ANODE POLARIZED—HEAVY COATING OF CORROSION PRODUCT

(2) 15 MIN. SOAK IN ELECT.—ANODE POLARIZED OUT WITH IMMEDIATE APPLICATION OF ANODIC CURRENT

TABLE I

EFFICIENCY BEHAVIOR - MIXED ACETATE - CHLORIDE ELECTROLYTES
AZ2IXI ANODES-70°F

% ANODE EFFICIENCY

ELECTROLYTE NORMALITY			CURRENT DENSITY – MA PER CM²					
Mg[AC]₂	$\frac{AC^-}{Cl^-}$	Mg Cl₂	1.6	3.1	5.4	7.9	15.5	30.3
2.0		0	78	82	87	90	88	80
2.0	400	.005	81	84	87	89	82	77
2.0	200	.01	81	83	85	83	75	73
2.0	40	.05	80	74	71	69	68	68
2.0	20	.10	78	69	68	68	67	67
2.0	4	.50	66	64	65	66	66	66
0		.50	65	63	64	66	66	66

TABLE II

EFFICIENCY BEHAVIOR—MIXED ACETATE — PERCHLORATE ELECTROLYTES

AZ21XI ANODES - 70°F

ELECTROLYTE NORMALITY Mg[AC]$_2$ — Mg[ClO$_4$]$_2$		$\dfrac{AC^-}{ClO_4^-}$	% ANODE EFFICIENCY CURRENT DENSITY–MA/CM^2				
Mg[AC]$_2$	Mg[ClO$_4$]$_2$		8.6	15	21	29	44
2.0	0		88	89			
2.0	0.5	4	87	90	88	86	80
0	2.5		77	79	78	78	77
0	1.0		77	75			
3.0	0		88	87			
3.0	2.0	1.5	85	84	83	81	81

TABLE III

EFFICIENCY BEHAVIOR – 2 NORMAL $Mg[ClO_4]_2$ ELECTROLYTES

ANODE CURRENT DENSITY – 15 MILLIAMPERES PER CM^2

ANODE COMPOSITION	NUMBER	% EFFICIENCY	
		UNTREATED ELECT.	*TREATED ELECT.
AZ21X1	91223	39	79
AZ21	94009	65	76

* TREATED WITH $Ag\,ClO_4$ AND ZINC POWDER

TABLE IV

OPEN CIRCUIT CORROSION

7 DAY STAGNANT IMMERSION

AZ2IXI ANODES — ALLOY No. 91223

ANODE SIZE – 2" x 2" x .146"

CORROSION RATE

SALT	NORMALITY	NO CHROMATE MCD(i)	.25 GMS/L Na_2CrO_4 MCD(i)
$MgCl_2$	6	2.67	.024
$Mg[ClO_4]_2$	6	.624	.006
$Mg[C_2H_3O_2]_2$	1	.041	.011
"	3	.132	.013
"	6	1.22	1.47
*$NH_4C_2H_3O_2$	2	18.5	17.4
"	4	26.8	27.6
"	6	29.5	29.6
$Ca[CHO_2]_2$	2	.184	.064

(i) MILLIGRAMS PER SQUARE CENTIMETER PER DAY

* 4 DAYS

TABLE V

TIME TO ONE VOLT POLARIZATION vs. CURRENT DENSITY

6 N Mg(ClO$_4$)$_2$ - AZ21X1 ANODES

Anode Area 0.80 cm^2± .04

Applied Current Milliamperes	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Seconds
805	1.01	1.16	0.86
876	1.10	.76	1.32
900	1.13	.79	1.26
900	1.13	.59	1.69
1.160	1.45	.31	3.22
1.170	1.46	.46	2.17
1.300	1.62	.37	2.70
1.400	1.75	.28	3.57

TABLE VI

EFFECT OF ELECTROLYTE SALT ON POLARIZATION PARAMETERS

6 NORMAL ELECTROLYTE – AZ2IXI ANODES

ELECTROLYTE SALT	CRITICAL CURRENT DENSITY AMPERES/CM^2	COULOMBS PER/CM^2
Mg[$ACl]_2$	0.015	2.2
$MgCl_2$	0.68	1.5
Mg[$ClO_4]_2$	0.73	0.3

TABLE VII

TIME TO ONE VOLT POLARIZATION vs. CURRENT DENSITY

AZ21X1 ANODES - ALLOY 91223 - 6.8 cm²

70F

1 Normal Mg(Ac)₂   2 N Mg(Ac)₂

Applied Current Milli- Amperes	Amps per cm²	Seconds to ΔE 1 Volt	1/Sec.	Applied Current Milli- Amperes	Amps per cm²	Seconds to ΔE 1 Volt	1/Sec.
1,950	.286	19.9	.05	800	did	not polarize	
2,100	.308	9.95	.10	920	.135	143	.007
2,510	.369	5.00	.20	970	.143	82.6	.012
2,780	.408	3.58	.28	1,090	.161	50.2	.020
2,790	.410	3.92	.26	1,130	.166	4.2	.024
2,800	.412	3.74	.27	1,290	.190	34.3	.029
2,830	.415	4.32	.23	1,420	.209	28.3	.035
3,020	.443	2.82	.36	1,500	.220	27.2	.037
3,290	.483	3.68	.27	1,640	.241	14.0	.071
3,370	.495	3.58	.28	1,700	.250	19.3	.052
3,370	.495	2.88	.35	2,030	.303	10.0	.100
3,410	.501	3.09	.32	2,110	.312	11.8	.085
3,620	.531	2.07	.48	2,280	.335	7.8	.128
3,700	.543	3.78	.36	4,300	.632	1.70	.571
4,590	.668	1.65	.60	4,800	.706	1.45	.690
4,820	.709	1.55	.64				
5,300	.778	1.02	.98				
5,330	.782	1.06	.94				
5,370	.789	1.09	.92				
5,400	.793	1.32	.76				
5,620	.825	1.00	1.0				

TABLE VIII

TIME TO ONE VOLT POLARIZATION vs. CURRENT DENSITY
AZ21X1 Anode - Alloy 91223 - 6.8 cm²
70F

3 N Mg(Ac)₂   4 N Mg(Ac)₂

Applied Current Milli-Amperes	Amps per cm²	Seconds to ΔE 1 Volt	1/Sec.	Applied Current Milli-Amperes	Amps per cm²	Seconds to ΔE 1 Volt	1/Sec.
360	did	not	polarize				
405							
445	.066	369	.0027	310	.045	344	.003
450	.066	292	.0034	355	.052	177	.006
460	.068	452	.0022	410	.060	107	.009
470	.069	262	.0034	460	.075	83	.012
470	.069	286	.0035	590	.086	47	.021
490	.072	272	.0037	650	.095	40	.025
495	.073	237	.0042	870	.128	19	.053
505	.074	226	.0044	855	.125	22	.045
520	.076	179	.0056	895	.131	21.3	.047
555	.082	180	.0055	900	.132	18.2	.055
585	.086	166	.0060	1,000	.147	14.1	.071
610	.090	150	.0067	1,070	.156	13.4	.075
620	.091	102	.0098	1,100	.162	11.5	.087
650	.095	113	.0088	1,220	.179	11.2	.089
705	.103	67	.0149	1,280	.188	10.2	.098
720	.106	87	.0115	1,330	.195	9.34	.107
815	.120	54.3	.0184	1,500	.220	7.8	.128
925	.136	37.8	.0264	1,800	.263	6.8	.147
1,020	.150	31.2	.0321	1,990	.292	5.36	.186
1,090	.160	27.9	.0358	3,140	.461	2.39	.418
1,180	.173	23.3	.0429	3,670	.538	1.0	1.000
1,310	.192	19.1	.0524	3,710	.545	1.67	.599
1,450	.213	15.5	.0645				

TABLE IX

TIME TO ONE VOLT POLARIZATION vs. CURRENT DENSITY

AZ21X1 Anodes - Alloy 91223 - 6.8 cm^2

5 N Mg(Ac)$_2$ - 70F

Applied Current Milliamperes	Amperes per cm^2	Seconds to ΔE 1 Volt	1/Seconds
150	Did	Not	Polarize
195	.029	359	.0028
245	.036	282	.0035
290	.042	132	.0076
330	.048	96.4	.0104
385	.055	68.6	.0146
445	.065	46.7	.0214
580	.071	32.7	.0306
645	.095	24.9	.0402
700	.103	24.7	.0405
785	.115	19.2	.0521
870	.128	15.4	.0649
940	.138	16.4	.0610
1,040	.153	13.2	.0758
1,090	.160	12.1	.0826
1,180	.173	9.9	.101
1,290	.190	10.7	.0934
1,300	.191	9.8	.1020
1,780	.261	6.1	.1639
2,580	.378	3.1	.3225
3,400	.500	2.4	.4167

TABLE X

EFFECT OF ELECTROLYTE CONCENTRATION ON POLARIZATION PARAMETERS

Mg [AC]$_2$ ELECTROLYTE – 70°F – AZ2IXI ANODES

	$1/N$	CRITICAL CURRENT AMPERES / CM^2	$1/$SLOPE COULOMBS/CM^2
NORMALITY			
1	1	0.27	0.6
2	.5	0.12	2.7
3	.33	.062	4.8
4	.25	.039	2.3
5	.20	.027	1.7
6	.17	.015	2.2

TABLE XI

TIME TO ONE VOLT POLARIZATION vs. CURRENT DENSITY
6 N Mg(Ac)$_2$ - Anode Area 6.8 cm^2 - 70F
Mg-Al Binaries

Alloy 94001

Pure Magnesium

Applied Current Milli-Amperes	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Sec.
830	.122	17.8	.056
830	.122	20.3	.049
890	.131	14.6	.068
935	.137	13.0	.077
950	.139	11.5	.087
1,020	.150	9.9	.101
1,040	.153	9.9	.101
1,100	.162	9.5	.105
1,200	.177	8.6	.116
1,400	.206-	5.2	.192

Alloy 94002
Mg+0.44%Al

Applied Current Milli-Amperes	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Sec.
565	.083	50.7	.020
630	.093	29.5	.034
745	.109	18.5	.054
810	.119	15.4	.065
1,000	.147	9.5	.105

Alloy 94008
Mg+4.8%Al

Applied Current Milli-Amperes	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Sec.
140	.021	Did Not Polarize	
185	.027	625	.0016
225	.033	267	.0037
290	.043	104	.0096
360	.053	54.8	.0182
460	.068	39.3	.0254
460	.068	38.4	.0260
500	.073	29.9	.0334

Alloy 94003

Mg+1.0%Al

Applied Current Milli-Amperes	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Sec.
210	.031	Did Not Polarize	
285	.040	248	.004
370	.054	73.2	.014
425	.063	60.4	.016
480	.071	43.1	.023
585	.086	28.4	.035
650	.096	22.6	.044
740	.109	18.3	.055
805	.118	14.1	.071
885	.130	11.1	.090

Alloy 94004
Mg+2.0%Al

Applied Current Milli-Amperes	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Sec.
160	.023	Did Not Polarize	
210	.031	451	.0022
305	.045	101	.0099
320	.047	79	.0126
370	.054	53	.0189
415	.061	45.9	.0218
445	.066	36	.0278
470	.069	37	.0274

TABLE XII

TIME TO ONE VOLT POLARIZATION vs. CURRENT DENSITY
6 N Mg(Ac)$_2$ - Anode Area 6.8 cm^2 - 70F
Mg-Zn Binaries

Alloy 94006
Mg+.23%Zn

Applied Current MA	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Sec.
675	.099	26.8	.037
680	.100	31.3	.032
750	.110	18.1	.055
820	.120	15.1	.066
890	.131	12.9	.077
935	.137	11.6	.086

Alloy 94007
Mg+.52%Zn

Applied Current MA	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Sec.
740	.109	21.8	.046
825	.121	15.0	.067
890	.131	12.9	.078
950	.139	11.2	.089
1,100	.162	8.2	.122
1,250	.184	7.6	.130
1,370	.203	3.1	.320

Alloy 94005
Mg+1%Zn

Applied Current MA	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Sec.
565	.083	Did Not Polarize	
605	.089	33	.030
740	.108	17.5	.057
835	.123	13.4	.074
850	.125	12.1	.083
935	.137	11.2	.089
985	.144	8.95	.112
1,100	.162	3.05	.328

TABLE XIII

TIME TO ONE VOLT POLARIZATION vs. CURRENT DENSITY

6 N Mg $[Ac]_2$ Anode Area 6.8 cm^2

Alloys

	Alloy 94009					Alloy 94010		
	AZ21+⟨01%Ca					AZ21+.036%Ca		
Applied Current MA	Amps per cm^2	Seconds to △E 1 Volt	1/Sec.		Applied Current MA	Amps per cm^2	Seconds to △E 1 Volt	1/Sec.
170	.025	Did Not Polarize			155	.023	322	.0031
200	.029	611	.0016		200	.029	157	.0064
245	.036	476	.0021		255	.038	96	.0104
295	.043	112	.0089		300	.044	71	.0141
345	.051	69	.0145		345	.051	57	.0175
450	.066	34	.0294					
	Alloy 94011					Alloy 94012		
	AZ21+0.14%Ca					AZ51		
105	.015	1,635	.0006		290	.043	100	.010
155	.023	271	.0037		345	.051	65	.015
205	.030	152	.0066		395	.058	49	.020
245	.036	113	.0088		445	.065	38.7	.026
285	.042	84	.0119		600	.088	24.1	.041
340	.050	65.2	.0153		735	.108	14.7	.068
	Alloy 91225							
	AZ31B-.44%Mn					AZ31 Low Mn		
195	.029	Did Not Polarize			100	.015	Did Not Polarize	
245	.036	356	.0028		150	.023	406	.0025
290	.043	156	.0064		200	.029	203	.0049
340	.050	81	.0123		245	.036	134	.0074
395	.058	58.6	.0171		245	.036	147	.0068
					290	.043	100	.0100
					345	.051	73.2	.0137

TABLE XIV

TIME TO ONE VOLT POLARIZATION vs. CURRENT DENSITY
6 N MgCl$_2$ - Anode Area 0.8 cm^2 - 70F
Mg-Al Binaries

Alloy 94001 Pure Magnesium				Alloy 94003 Mg+1.0%Al			
Applied Current MA	Amps per cm^2	Seconds to ΔE 1 Volt	1/Sec.	Applied Current MA	Amps per cm^2	Seconds to ΔE 1 Volt	1/Sec.
715	.89	7.4	.135	515	.64	126	.008
760	.95	6.6	.152	590	.74	20	.050
775	.96	4.6	.217	660	.82	11.2	.089
800	1.0	5.5	.181	740	.92	6.4	.156
840	1.05	4.5	.222	820	1.02	4.6	.217
890	1.11	3.6	.278	900	1.12	3.1	.323

Alloy 94002 Mg+0.5%Al				Alloy 94004 Mg+2.0%Al			
530	.66	30.1	.033	495	.62	129	.0077
595	.74	13.5	.074	520	.65	38.9	.026
660	.82	9.6	.104	590	.74	21.7	.046
740	.92	5.8	.172	665	.83	8.7	.115
805	1.01	4.8	.208	740	.93	5.8	.172
895	1.12	2.8	.357	815	1.02	4.0	.250

Alloy 94008 Mg+4.8%Al			
490	.61	69.8	.014
580	.73	23.1	.043
660	.83	10.0	.100
740	.93	5.3	.189
800	1.0	3.6	.278
910	1.14	2.0	.500

TABLE XV

TIME TO ONE VOLT POLARIZATION vs. CURRENT DENSITY
6 N MgCl$_2$ - Anode Area 0.8 cm^2 - 70F
Mg-Zn Binaries

Alloy 94006 Mg+.23%Zn

Applied Current MA	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Sec.
760	.95	4.66	.215
820	1.02	4.93	.203
850	1.06	3.3	.303
925	1.15	1.83	.546
985	1.23	1.73	.578

Alloy 94007 Mg+0.52%Zn

Applied Current MA	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Sec.
635	.79	113	.009
660	.82	136	.007
725	.90	6.5	.154
775	.97	5.64	.177
845	1.05	3.25	.308
925	1.15	2.52	.396

Alloy 94005 Mg+1.0%Zn

Applied Current MA	Amps per cm^2	Seconds to $\triangle$E 1 Volt	1/Sec.
625	.78	219	.004
660	.82	13.3	.075
760	.95	5.74	.174
815	1.02	3.4	.294
910	1.13	4.3	.232

TABLE XVI

TIME TO ONE VOLT POLARIZATION vs. CURRENT DENSITY
6 N MgCl$_2$ - Anode Area 0.8 cm^2 - 70F
Alloys

Alloy 94009 AZ21-⟨.01%Ca				Alloy 94010 AZ21-.036%Ca			
Applied Current MA	Amps per cm^2	Seconds to $\triangle E$ 1 Volt	1/Sec.	Applied Current MA	Amps per cm^2	Seconds to $\triangle E$ 1 Volt	1/Sec.
515	.64	22.9	.044	480	.66	50.5	.020
605	.76	13.1	.076	575	.72	12.9	.078
680	.85	6.0	.167	645	.80	7.2	.139
750	.93	3.84	.260	740	.92	4.37	.229
820	1.02	2.54	.394	820	1.02	2.66	.376
905	1.13	1.45	.690	915	1.14	1.57	.637

Alloy 94011 AZ21+.14%Ca				Alloy 94012 AZ51			
500	.62	36.9	.027	500	.62	80.6	.012
580	.73	15.0	.067	550	.69	30.7	.032
660	.82	7.1	.141	605	.75	21.3	.047
740	.93	3.44	.291	695	.87	3.98	.251
840	1.05	1.50	.667	785	.98	3.45	.298
920	1.15	1.12	.893	900	1.12	1.00	1.00

Alloy 91225 AZ31B-.44%Mn				Alloy 94887 AZ31 - low Mn			
485	.61	47.8	.021	550	.69	28.1	.036
550	.69	14.8	.068	650	.81	8.3	.120
610	.76	8.5	.118	740	.92	4.4	.227
665	.83	4.8	.208	820	1.03	3.0	.333
745	.93	3.6	.278	925	1.15	1.9	.526
835	1.04	2.3	.435				
935	1.17	1.3	.769				

TABLE XVII

THE EFFECT OF ANODE COMPOSITION ON POLARIZATION PARAMETERS

ALLOY No.	Al	Ca	Mn	Zn		CRITICAL CURRENT AMPERES / CM²		SLOPE−1 COULOMBS/CM²	
						6 N Mg [AC]₂ −6N MgCl₂	6N MgCl₂	6 N Mg[AC]₂ −6N MgCl₂	6N MgCl₂
94001	<.03	<.01	<.01	.001	BLANK	.089	0.76	0.6	1.4
94002	.51	<.01	<.01	.001	EFFECT OF Al	.067	0.63	0.74	1.6
94003	1.02	"	"	"		.034	0.64	1.5	1.7
94004	1.99	"	"	"		.028	0.64	1.5	1.5
94008	4.88	"	"	"		.025	0.63	1.6	1.4
94006	.003	<.01	<.01	.23	EFFECT OF Zn	.074	0.75	0.7	0.9
94007	"	"	"	.52		.074	0.78	0.7	0.9
94005	"	"	"	1.0		.071	0.73	0.7	1.1
94009	1.9	<.01	.022	1.19	EFFECT OF Ca, Al and Zn	.028	0.62	1.6	1.0
94010	1.9	.036	.013	1.15		.017	0.60	2.0	1.2
94011	2.0	.14	.015	1.25		.014	0.61	2.5	1.2
94012	5.2	<.01	.016	1.08	Al & Zn	.027	0.62	1.3	1.2
94887	3.2	.03	.01	0.93		.017	0.65	2.5	1.1
91225	2.9	<.01	.43	0.94		.032	0.62	1.7	1.0

TABLE XVIII

INTERGRANULAR CORROSION
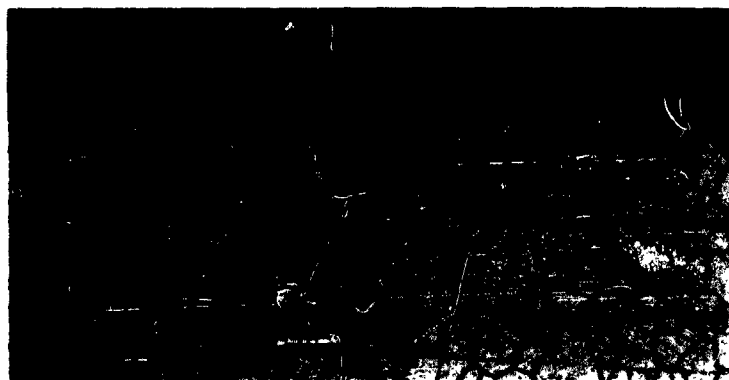
250X - Acetic Picral Etch
Neg. No. 52783
AZ21X1 - Corroded in 2N $Mg[ClO_4]_2$

250X - Acetic Picral Etch
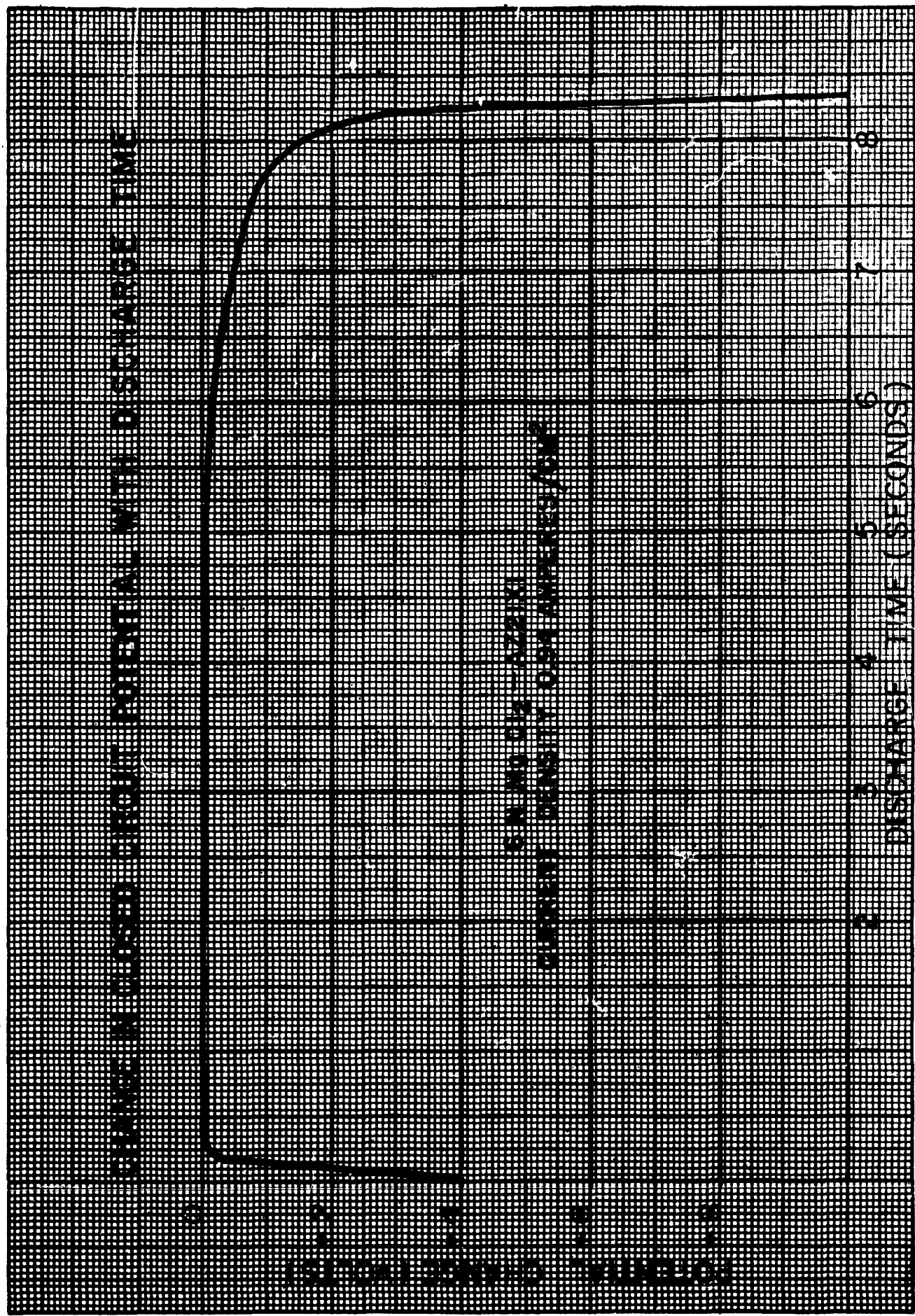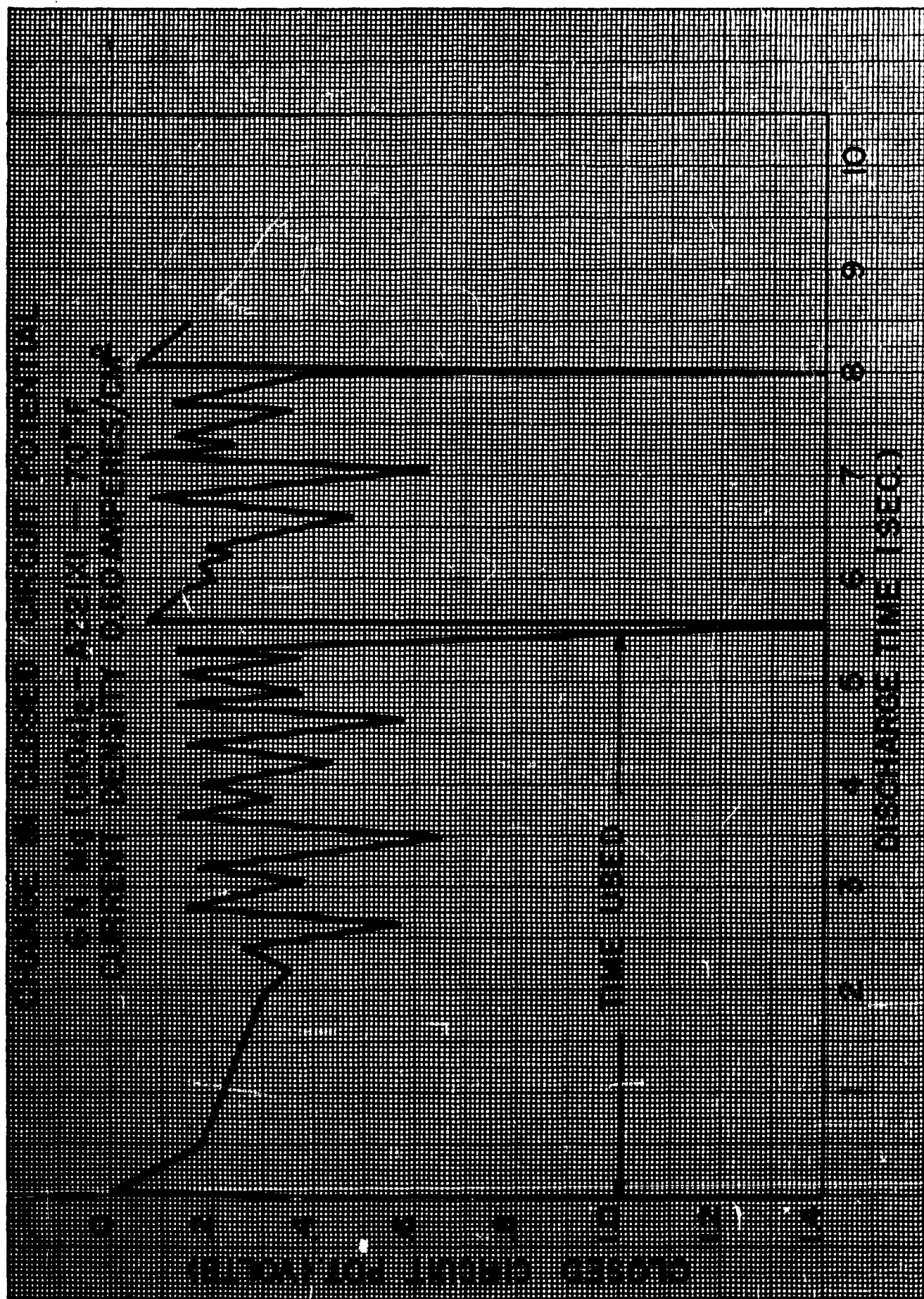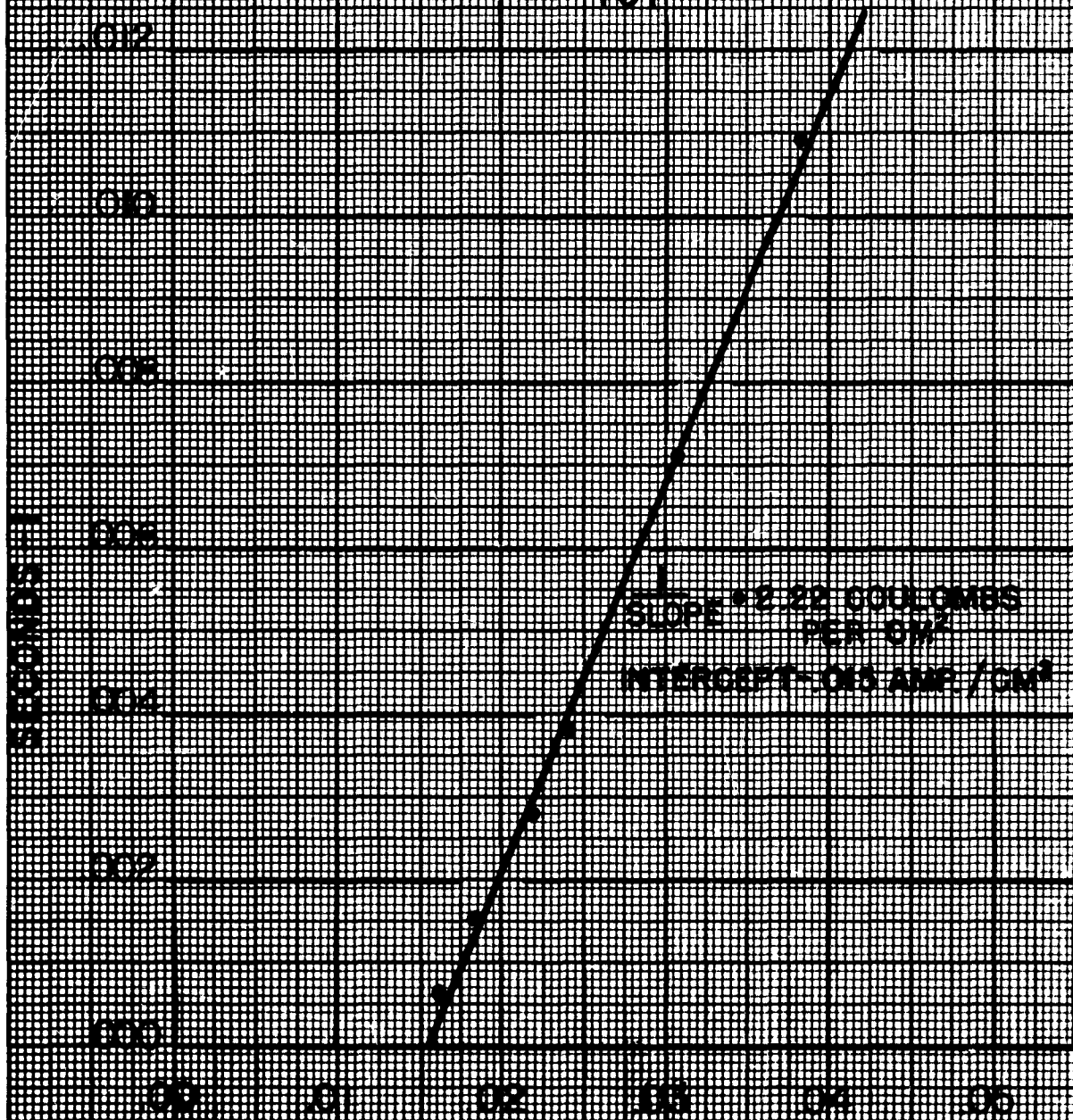Neg. No. 52744
AZ10XA - Corroded in 1N $Mg[ClO_4]_2$

Figure 1

CHANGE IN CLOSED CIRCUIT POTENTIAL WITH DISCHARGE TIME

BATTERY OZ-2X2X1
CURRENT DENSITY 0.04 AMPERES/IN²

DISCHARGE TIME (SECONDS)

FIG. 2

FIG. 3

RECIPROCAL TIME FOR POLARIZATION vs
CURRENT DENSITY
6 N Mg [AC]₂ - AZ21XI
70 F

SLOPE = 2.22 COULOMBS
PER CM²
INTERCEPT = .045 AMP / CM²

SECONDS⁻¹

CURRENT DENSITY - AMPERES / CM²

FIG.

DIFFUSION DIFFUSION [...] POLARIZATION vs CURRENT DENSITY

GI/NaCl = 70 F

472 = 0.95 × 00 = 0.05

MG/CM² = AMPERES/CM²

MG/CM² = 12 COULOMBS/AMPERE

AMPERES/CM²

FIG. 5

0.2   0.4   0.6   0.8   10   11   12

DIFFUSION | × 10²
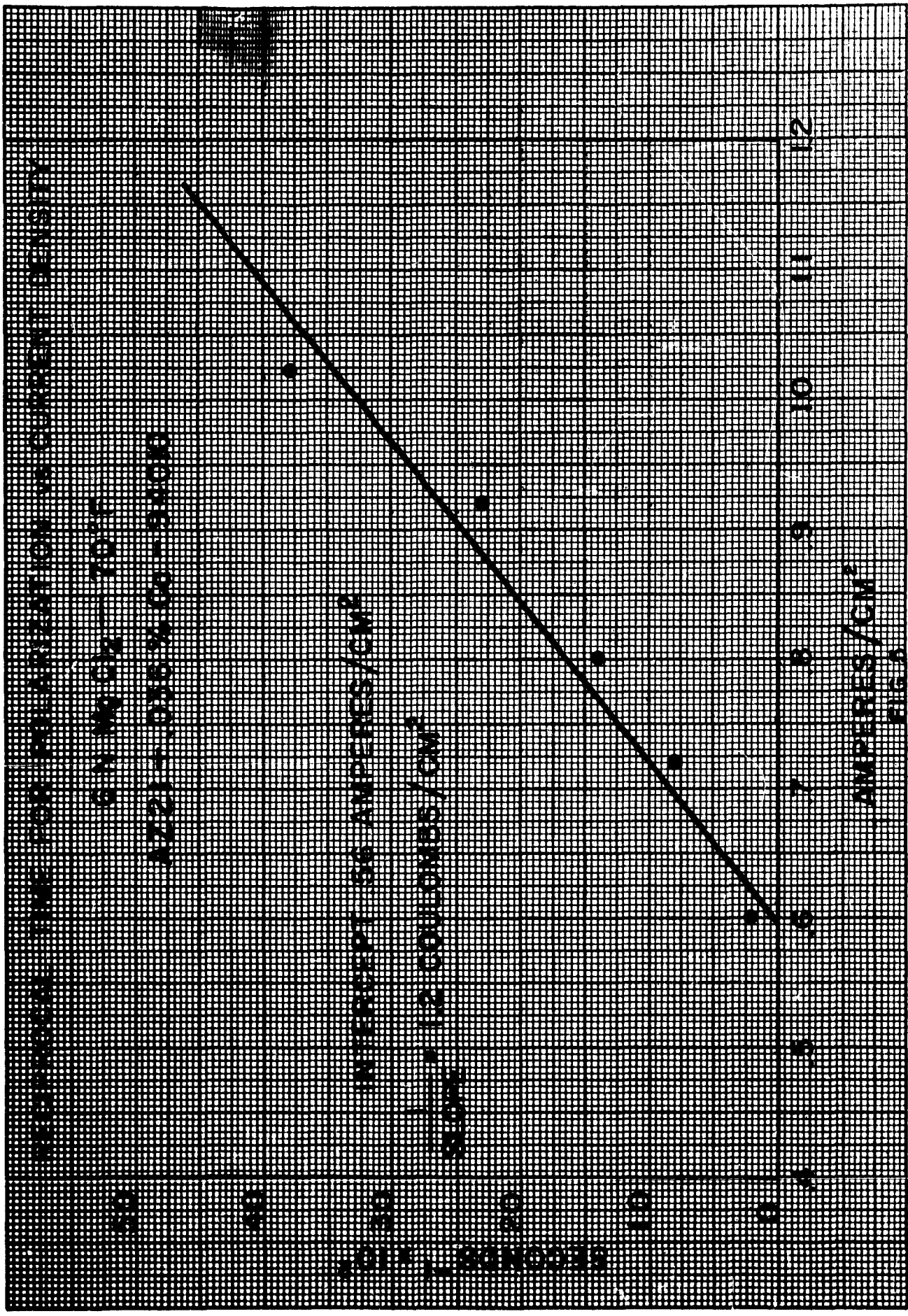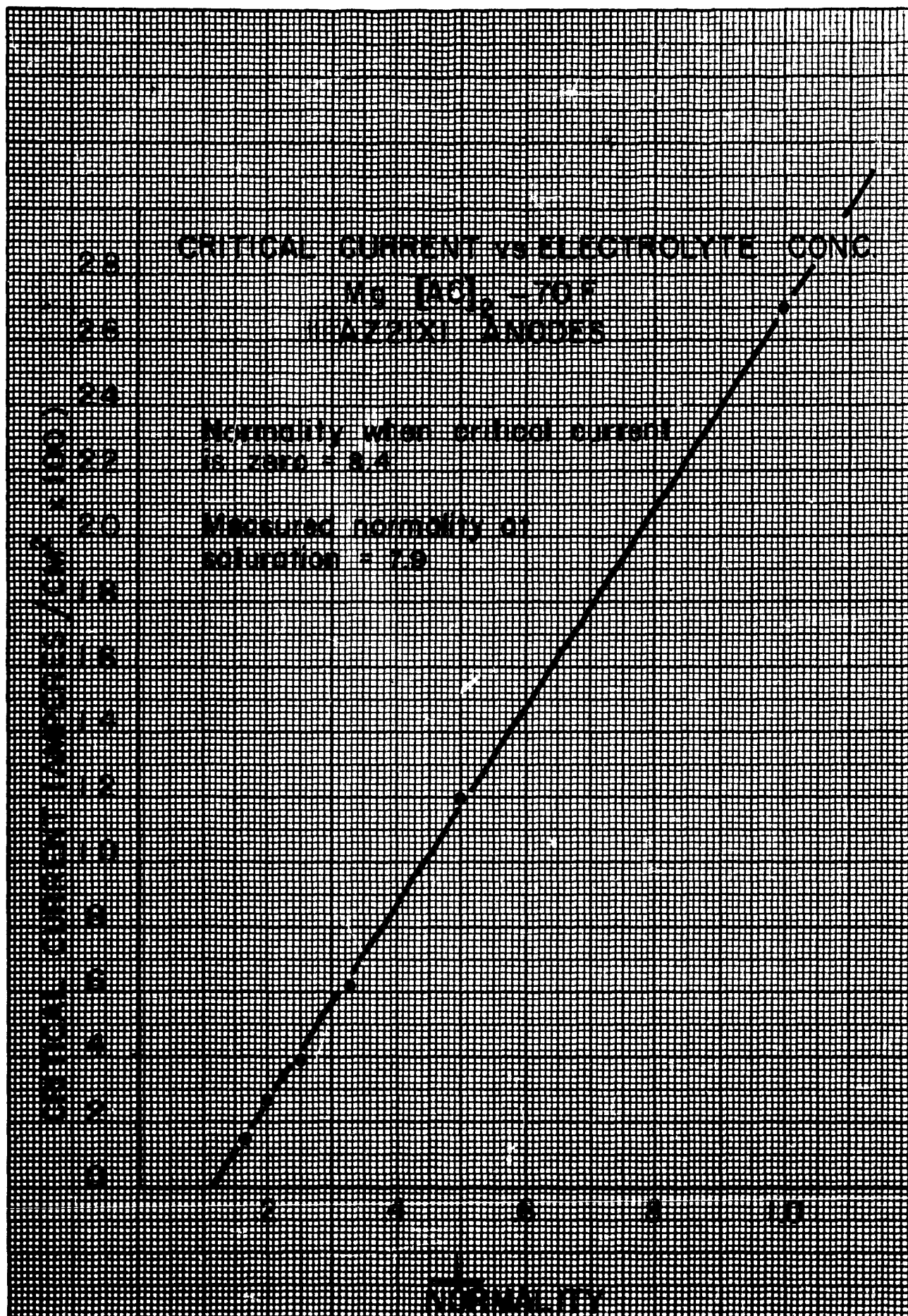
FIG. 6

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